metal-organic compounds

catena-Poly[[triaquachlorido-*µ*₃-malonato-cerium(III)] hemihydrate]

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The asymmetric unit of the title compound, {[Ce(C₃H₂O₄)Cl-(H₂O)₃]·0.5H₂O}ₙ, contains a Ce³⁺ atom coordinated by a chloride anion, three water molecules and a malonate ligand, and one water molecule of crystallization with a factor of occupancy of 50%. The malonate ligand is bonded to three different symmetry-related metal atoms yielding a one-dimensional coordination polymer running parallel to the *a* axis. A supramolecular network composed of strong and highly directional O—H···O and O—H···Cl hydrogen bonds ensures a close and effective packing of adjacent polymeric chains.

Related literature

For general background to coordination compounds of malonates with lanthanides, see: Cañadillas-Delgado *et al.* (2006); Doreswamy *et al.* (2003, 2005); Hernández-Molina *et al.* (2000, 2002, 2003). For previous research from our group on coordination compounds of phosphonates, see: Cunha-Silva *et al.* (2007, 2009); Shi *et al.* (2008); Paz *et al.* (2004, 2005). For general background to the synthesis of coordination polymers using microwave heating, see: Klinowski *et al.* (2010).
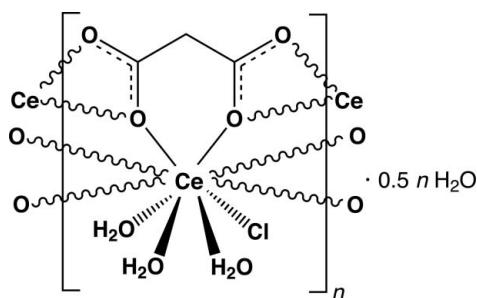
Experimental

Crystal data

[Ce(C₃H₂O₄)Cl(H₂O)₃]·0.5H₂O
M_r = 681.34
Monoclinic, $P2_1/c$
a = 7.6340 (2) Å
b = 14.3065 (3) Å
c = 8.7370 (2) Å
β = 99.949 (1)°

V = 939.87 (4) Å³
Z = 2
Mo $K\alpha$ radiation
μ = 5.13 mm⁻¹
T = 150 K
0.26 × 0.16 × 0.16 mm

Data collection

Bruker X8 Kappa CCD APEXII diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
T_{min} = 0.349, T_{max} = 0.494

8271 measured reflections
2514 independent reflections
2481 reflections with $I > 2\sigma(I)$
R_{int} = 0.028

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.021
$wR(F^2)$ = 0.053
S = 1.17
2514 reflections
143 parameters
12 restraints

H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.46 e Å⁻³
$\Delta\rho_{min}$ = −1.77 e Å⁻³

Table 1
Selected bond lengths (Å).

Ce1—O1W	2.4580 (17)	Ce1—O2^i	2.6083 (16)
Ce1—O3	2.4940 (16)	Ce1—O3^{ii}	2.6304 (17)
Ce1—O3W	2.5525 (18)	Ce1—O4^{ii}	2.6487 (18)
Ce1—O1	2.5683 (16)	Ce1—O1^i	2.6793 (18)
Ce1—O2W	2.5895 (17)	Ce1—Cl1	2.9086 (6)

Symmetry codes: (i) $-x + 2, -y, -z + 2$; (ii) $-x + 1, -y, -z + 2$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1X···Cl1^{iii}	0.94 (1)	2.20 (2)	3.0967 (18)	159 (2)
O1W—H1Y···O2^{iv}	0.94 (1)	1.71 (1)	2.652 (2)	174 (3)
O2W—H2X···Cl1^i	0.94 (1)	2.11 (3)	3.0416 (19)	171 (3)
O2W—H2Y···O4W^v	0.94 (1)	1.94 (2)	2.816 (3)	153 (3)
O2W—H2Y···O4W	0.94 (1)	2.00 (2)	2.793 (4)	141 (3)
O3W—H3X···O4^{vi}	0.95 (1)	1.86 (1)	2.798 (2)	173 (3)
O3W—H3Y···O2W^{ii}	0.95 (3)	1.85 (3)	2.794 (3)	173 (3)
O4W—H4X···Cl1^{ii}	0.95 (1)	2.38 (1)	3.326 (4)	176 (6)
O4W—H4Y···O4W^{vii}	0.95 (1)	2.26 (4)	3.083 (4)	144 (5)

Symmetry codes: (i) $-x + 2, -y, -z + 2$; (ii) $-x + 1, -y, -z + 2$; (iii) $x, -y - \frac{1}{2}, z - \frac{1}{2}$; (iv) $-x + 2, y - \frac{1}{2}, -z + \frac{5}{2}$; (v) $-x + 1, -y, -z + 1$; (vi) $-x + 1, y - \frac{1}{2}, -z + \frac{5}{2}$; (vii) $x, y, z - 1$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT-Plus* (Bruker, 2005); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg, 2009); software used to prepare material for publication: *SHELXTL*.

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supporting information

catena-Poly[[triaquachlorido-*μ₃*-malonato-cerium(III)] hemihydrate]

Patrícia Silva, José A. Fernandes and Filipe A. Almeida Paz

S1. Comment

The hydro-ionothermal reaction between tetraethyl-*p*-xylylenebisphosphonate (texbp) and CeCl$_3$·6H$_2$O in pre-prepared homogeneous eutectic mixtures of choline chloride and malonic acid is known to lead to the phase-pure crystalline material [Ce(Hpmd)(H$_2$O)] [where H$_4$pmd is 1,4-phenylenebis(methylene)diphosphonic acid, the hydrolysis product of texbp] (Shi *et al.*, 2008). Following our continuous interest in the preparation and study of the properties of metal-organic frameworks based on phosphonates (Cunha-Silva *et al.*, 2009; Cunha-Silva *et al.*, 2007; Paz *et al.*, 2005; Paz *et al.*, 2004), and our recent motivation to employ microwaves as an alternative heating source (Klinowski *et al.*, 2010), we decided to test the aforementioned synthetic conditions inside a microwave reactor. The use of microwave heating instead of hydro-ionothermal conditions resulted instead in the isolation of the title compound as a by-product, being composed of a one-dimensional polymer of Ce^{3+} with malonate residues. Noteworthy, this organic ligand can be found in a number of structures comprising lanthanide centres (Cañadillas-Delgado *et al.*, 2006; Hernández-Molina *et al.*, 2000; Hernández-Molina *et al.*, 2002; Hernández -Molina *et al.*, 2003; Doreswamy *et al.*, 2003; Doreswamy *et al.* 2005) exhibiting several types of coordination modes such as unidentate, chelating and bridging.

   The asymmetric unit of the title compound (see Scheme) comprises a chlorido, three water and one malonato (mal^{2-}) entities coordinated to Ce^{3+}, and one half-occupied water molecule of crystallization located in a generic crystallographic position: [CeCl(mal)(H$_2$O)$_3$]·0.5(H$_2$O). The coordination geometry of the metallic centre can be described as a highly distorted dodecahedron (Figure 1). For example, while the Ce1—O$_{water}$ distances range from 2.4580 (17) to 2.5895 (17) Å (see Table 1), the Ce1—Cl1 bond is considerably longer [2.9086 (6) Å]. The malonate ligand is, on the one hand, bound to the central Ce^{3+} *via* distal Ce—O bonds [distances of 2.5683 (16) and 2.4940 (16) Å], leading to the formation of a six-membered chelate ring. On the other, each carboxylate establishes a physical connection with a neighbouring metallic centre *via* proximal chelations [Ce—O distances in the 2.6083 (16) to 2.6793 (18) Å range - see Table 1], thus forming the four-membered chelate rings depicted in the chemical diagram. These two different coordination modes of the malonate ligand lead to the formation of a one-dimensional coordination polymer running parallel to the [100] direction (Figure 2). The intermetallic distances within the polymer are of 4.3832 (2) and 4.5091 (2) Å.

   Due to the large number of donors and acceptors, the crystal structure of the title compound is rich in strong [D···A distances in the 2.652 (2)–3.326 (4) Å range] and highly directional [⟨ D—H···A larger than *ca* 141 (3)°] hydrogen bonds (see Table 2). The hydrogen bonding interactions can be divided in three different types concerning the connectivity in relation to the polymeric chain. Intra-chain hydrogen bonds add stability to the coordination polymer by connecting three adjacent metal centres through a O3W···O2W···Cl chain (blue dashed lines in Figure 2). The other two types of hydrogen bonds involve the crystal packing of adjacent coordination polymers: inter-chain interactions (green dashed lines in Figures 2 and 3) connect coordinated water molecules (O1W and O3W) of one polymer to the oxygen atoms of malonato ligands (O2 and O4, respectively) of an adjacent polymer; the second type of inter-chain interactions occur *via* the half-occupied crystallization water molecule (O4W) forming O4···O4W···Cl1 chains (pink dashed lines in Figures 2 and 3).

The extensive hydrogen bonding network described above leads to a series of strong connections among adjacent coordination polymers as depicted in Figure 3.

S2. Experimental

The title compound was prepared following the procedure described elsewhere (Shi *et al.*, 2008), while replacing hydro-thermal heating by microwave heating (Klinowski *et al.*, 2010). The reactive homogeneous suspension was transferred to a 10 ml IntelliVent reactor which was placed inside a CEM Focused Microwave™ Synthesis System Discover S-Class equipment. The reaction took place with constant magnetic stirring (controlled by the microwave equipment) and by monitoring the temperature and pressure inside the vessel. Experimental conditions: i) temperature of 120 °C; ii) power of 50 W; iii) reaction time of 45 minutes of microwave irradiation. A constant flow of air (*ca* 10 psi) ensured a close control of the temperature inside the vessel. After reacting a colourless solution was obtained. The resulting solution was then left to stand at ambient temperature until large block crystals grew by slow evaporation of the solvent over a period of six months.

S3. Refinement

C-bound H atoms were located at their idealized positions and were included in the final structural model in riding-motion approximation with C—H distances of 0.99 Å. The isotropic displacement parameters for these atoms were fixed at $1.2 \times U_{eq}$ of the carbon atom to which they are attached.

All hydrogen atoms associated with the water molecules were directly located from difference Fourier maps and included in the structure with the O—H and H···H distances restrained to 0.95 (1) and 1.55 (1) Å, and with U_{iso} fixed at $1.5 \times U_{eq}$ of the O atom to which they are attached.
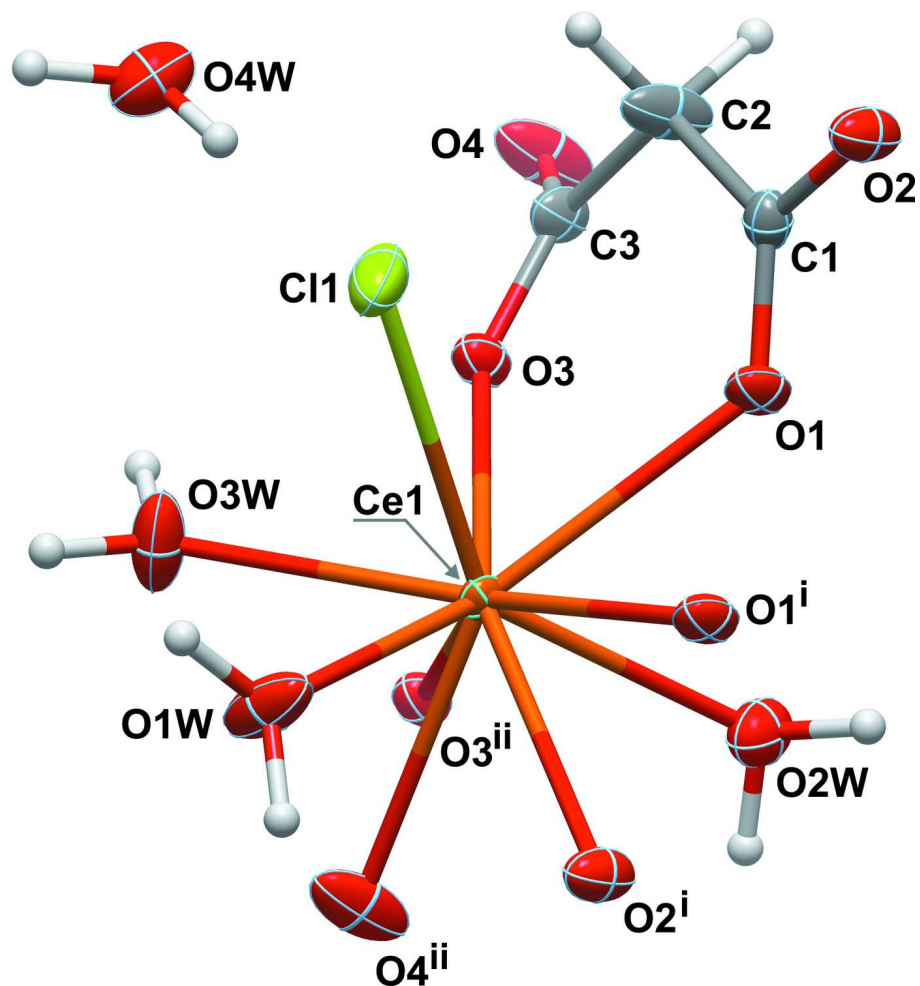
Figure 1
Asymmetric unit of the title compound showing all non-hydrogen atoms as displacement ellipsoids drawn at the 50% probability level and hydrogen atoms as small spheres with arbitrary radius [symmetry codes: (i)2 - *x*, -*y*, 2 - *z*; (ii)1 - *x*, -*y*, 2 - *z*]. The water molecule of crystallization, with fractional occupancy, is also depicted. For clarity, the coordination sphere of Ce1 was completed by generating by symmetry the remaining oxygen atoms.

Figure 2

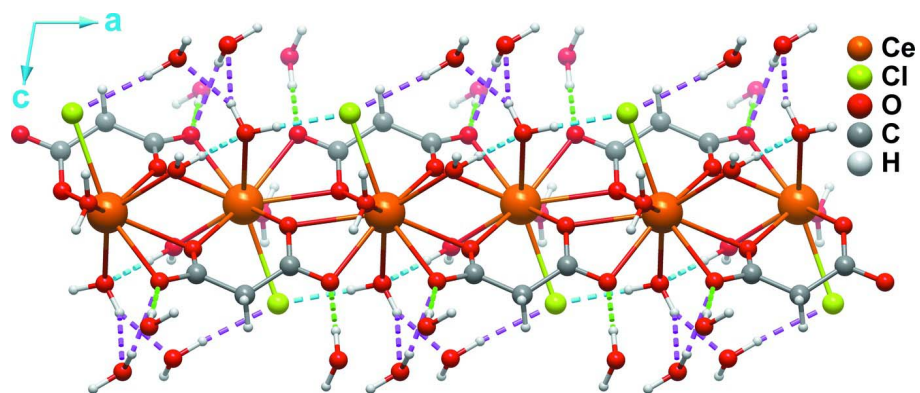Schematic representation of the one-dimensional chain coordination polymer composing the crystal structure of the title compound. Hydrogen bonds are represented as dashed lines: **blue** - intra-chain interactions; **pink** - hydrogen bonds with the water molecule of crystallization O4W; **green** - inter-chain interactions establishing direct supramolecular connections between adjacent polymers.
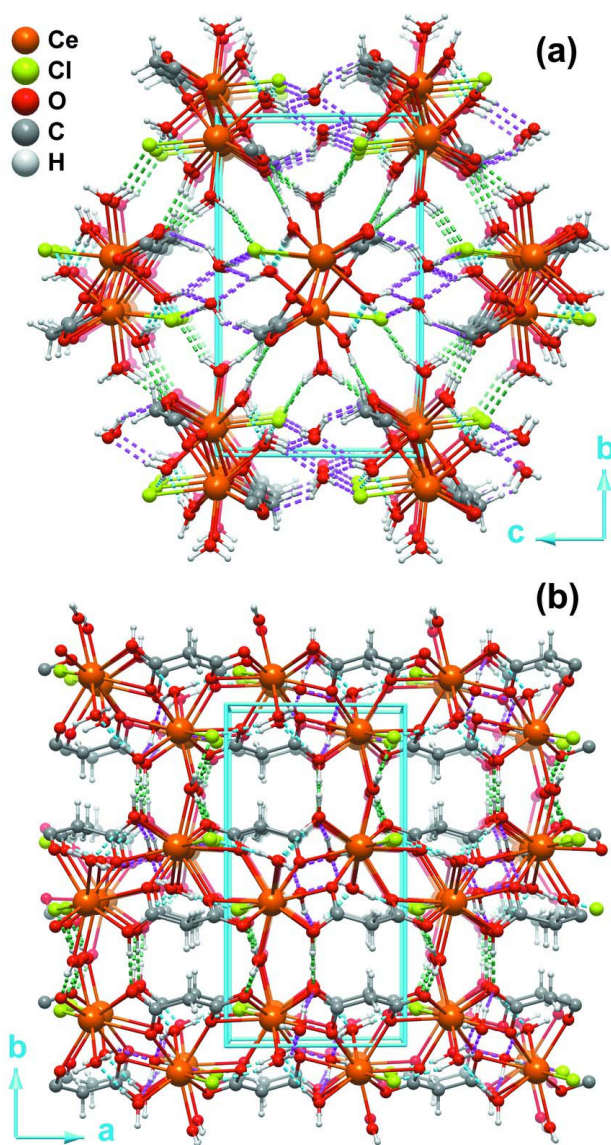
Figure 3

Crystal packing viewed in perspective along the **(a)** [100] and **(b)** [001] directions of the unit cell. Hydrogen bonds represented as in Figure 2.

catena-Poly[[triaquachlorido-μ_3-malonato-cerium(III)] hemihydrate]

Crystal data

$[Ce(C_3H_2O_4)Cl(H_2O)_3]\cdot0.5H_2O$	$F(000) = 648$
$M_r = 681.34$	$D_x = 2.408$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 6974 reflections
$a = 7.6340$ (2) Å	$\theta = 3.1–29.1°$
$b = 14.3065$ (3) Å	$\mu = 5.13$ mm^{-1}
$c = 8.7370$ (2) Å	$T = 150$ K
$\beta = 99.949$ (1)°	Block, colourless
$V = 939.87$ (4) Å^3	$0.26 \times 0.16 \times 0.16$ mm
$Z = 2$	

Data collection

Bruker X8 Kappa CCD APEXII diffractometer	8271 measured reflections
Radiation source: fine-focus sealed tube	2514 independent reflections
Graphite monochromator	2481 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.028$
Absorption correction: multi-scan ($SADABS$; Sheldrick, 1998)	$\theta_{max} = 29.1°$, $\theta_{min} = 3.7°$
	$h = -7 \rightarrow 10$
	$k = -19 \rightarrow 18$
$T_{min} = 0.349$, $T_{max} = 0.494$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.021$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.053$	
$S = 1.17$	$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2 + 1.2954P]$
2514 reflections	where $P = (F_o^2 + 2F_c^2)/3$
143 parameters	$(\Delta/\sigma)_{max} = 0.001$
12 restraints	$\Delta\rho_{max} = 1.46$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -1.77$ e Å^{-3}
	Extinction correction: $SHELXTL$ (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0139 (5)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ce1	0.742523 (15)	−0.079259 (8)	0.986480 (14)	0.00713 (7)	
Cl1	0.93077 (9)	−0.10017 (4)	1.30370 (7)	0.01792 (13)	
O1	0.9184 (2)	0.07240 (11)	1.0558 (2)	0.0110 (3)	
O2	1.1044 (2)	0.14538 (12)	1.23544 (19)	0.0126 (3)	
O3	0.5892 (2)	0.03721 (11)	1.12981 (19)	0.0100 (3)	
O4	0.4894 (2)	0.16117 (13)	1.2331 (2)	0.0187 (4)	
C1	0.9494 (3)	0.11752 (15)	1.1829 (3)	0.0089 (4)	
C2	0.8055 (3)	0.14023 (19)	1.2763 (3)	0.0166 (5)	
H2A	0.8375	0.1100	1.3793	0.020*	
H2B	0.8066	0.2086	1.2938	0.020*	
C3	0.6181 (3)	0.11199 (16)	1.2087 (3)	0.0113 (4)	
O1W	0.8161 (3)	−0.24629 (12)	1.0159 (2)	0.0186 (4)	
H1X	0.844 (5)	−0.2811 (19)	0.932 (2)	0.028*	
H1Y	0.844 (5)	−0.2812 (19)	1.1084 (19)	0.028*	
O2W	0.7066 (2)	0.03997 (12)	0.7602 (2)	0.0139 (3)	

H2X	0.815 (2)	0.065 (2)	0.740 (3)	0.021*	
H2Y	0.635 (3)	0.021 (2)	0.667 (2)	0.021*	
O3W	0.5195 (3)	−0.16461 (12)	1.1230 (2)	0.0185 (4)	
H3X	0.518 (5)	−0.2259 (10)	1.164 (4)	0.028*	
H3Y	0.439 (4)	−0.1266 (17)	1.167 (4)	0.028*	
O4W	0.4133 (5)	0.0545 (3)	0.5211 (4)	0.0186 (7)	0.50
H4X	0.318 (7)	0.066 (4)	0.576 (8)	0.028*	0.50
H4Y	0.435 (9)	0.109 (3)	0.465 (7)	0.028*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ce1	0.00713 (9)	0.00740 (9)	0.00779 (9)	−0.00056 (4)	0.00394 (5)	−0.00129 (3)
Cl1	0.0202 (3)	0.0217 (3)	0.0116 (3)	−0.0073 (2)	0.0020 (2)	0.0043 (2)
O1	0.0114 (8)	0.0119 (7)	0.0108 (8)	−0.0008 (6)	0.0051 (6)	−0.0046 (6)
O2	0.0086 (8)	0.0182 (8)	0.0116 (7)	−0.0021 (6)	0.0034 (6)	−0.0050 (6)
O3	0.0094 (8)	0.0096 (7)	0.0118 (7)	−0.0012 (6)	0.0040 (6)	−0.0031 (6)
O4	0.0094 (8)	0.0192 (8)	0.0285 (10)	0.0005 (7)	0.0062 (7)	−0.0146 (7)
C1	0.0091 (10)	0.0076 (9)	0.0108 (9)	0.0003 (7)	0.0038 (8)	0.0005 (7)
C2	0.0078 (11)	0.0253 (12)	0.0180 (11)	−0.0024 (9)	0.0061 (9)	−0.0128 (10)
C3	0.0095 (10)	0.0140 (10)	0.0118 (10)	−0.0024 (8)	0.0062 (8)	−0.0034 (8)
O1W	0.0330 (11)	0.0132 (8)	0.0111 (8)	0.0097 (8)	0.0078 (7)	0.0013 (6)
O2W	0.0112 (8)	0.0178 (8)	0.0133 (8)	−0.0016 (6)	0.0036 (6)	0.0001 (6)
O3W	0.0198 (9)	0.0112 (7)	0.0288 (10)	0.0021 (7)	0.0159 (8)	0.0049 (7)
O4W	0.0189 (19)	0.0240 (18)	0.0134 (16)	0.0028 (16)	0.0043 (14)	0.0011 (14)

Geometric parameters (Å, º)

Ce1—O1W	2.4580 (17)	O3—Ce1^{ii}	2.6304 (17)
Ce1—O3	2.4940 (16)	O4—C3	1.256 (3)
Ce1—O3W	2.5525 (18)	O4—Ce1^{ii}	2.6487 (18)
Ce1—O1	2.5683 (16)	C1—C2	1.512 (3)
Ce1—O2W	2.5895 (17)	C1—Ce1^{i}	3.038 (2)
Ce1—O2^{i}	2.6083 (16)	C2—C3	1.505 (3)
Ce1—O3^{ii}	2.6304 (17)	C2—H2A	0.9900
Ce1—O4^{ii}	2.6487 (18)	C2—H2B	0.9900
Ce1—O1^{i}	2.6793 (18)	C3—Ce1^{ii}	3.014 (2)
Ce1—Cl1	2.9086 (6)	O1W—H1X	0.943 (10)
Ce1—C3^{ii}	3.014 (2)	O1W—H1Y	0.943 (10)
Ce1—C1^{i}	3.038 (2)	O2W—H2X	0.944 (10)
O1—C1	1.271 (3)	O2W—H2Y	0.941 (10)
O1—Ce1^{i}	2.6793 (18)	O3W—H3X	0.947 (10)
O2—C1	1.258 (3)	O3W—H3Y	0.95 (3)
O2—Ce1^{i}	2.6083 (16)	O4W—H4X	0.947 (10)
O3—C3	1.271 (3)	O4W—H4Y	0.947 (10)
O1W—Ce1—O3	135.69 (6)	O3^{ii}—Ce1—C3^{ii}	24.86 (5)
O1W—Ce1—O3W	69.19 (6)	O4^{ii}—Ce1—C3^{ii}	24.56 (6)

O3—Ce1—O3W	71.11 (5)	O1ⁱ—Ce1—C3ⁱⁱ	137.52 (6)
O1W—Ce1—O1	134.11 (7)	Cl1—Ce1—C3ⁱⁱ	140.88 (5)
O3—Ce1—O1	65.71 (5)	O1W—Ce1—C1ⁱ	72.16 (6)
O3W—Ce1—O1	131.12 (6)	O3—Ce1—C1ⁱ	146.63 (6)
O1W—Ce1—O2W	135.43 (6)	O3W—Ce1—C1ⁱ	140.97 (6)
O3—Ce1—O2W	86.92 (5)	O1—Ce1—C1ⁱ	81.37 (6)
O3W—Ce1—O2W	132.90 (6)	O2W—Ce1—C1ⁱ	74.66 (6)
O1—Ce1—O2W	66.78 (6)	O2ⁱ—Ce1—C1ⁱ	24.25 (6)
O1W—Ce1—O2ⁱ	66.52 (6)	O3ⁱⁱ—Ce1—C1ⁱ	128.90 (6)
O3—Ce1—O2ⁱ	157.66 (5)	O4ⁱⁱ—Ce1—C1ⁱ	92.55 (6)
O3W—Ce1—O2ⁱ	126.49 (6)	O1ⁱ—Ce1—C1ⁱ	24.68 (6)
O1—Ce1—O2ⁱ	101.46 (5)	Cl1—Ce1—C1ⁱ	98.57 (4)
O2W—Ce1—O2ⁱ	70.93 (5)	C3ⁱⁱ—Ce1—C1ⁱ	113.88 (6)
O1W—Ce1—O3ⁱⁱ	116.75 (6)	C1—O1—Ce1	130.24 (15)
O3—Ce1—O3ⁱⁱ	62.43 (6)	C1—O1—Ce1ⁱ	93.64 (14)
O3W—Ce1—O3ⁱⁱ	67.32 (6)	Ce1—O1—Ce1ⁱ	118.46 (6)
O1—Ce1—O3ⁱⁱ	109.09 (5)	C1—O2—Ce1ⁱ	97.36 (13)
O2W—Ce1—O3ⁱⁱ	65.58 (5)	C3—O3—Ce1	141.45 (15)
O2ⁱ—Ce1—O3ⁱⁱ	108.72 (5)	C3—O3—Ce1ⁱⁱ	94.72 (14)
O1W—Ce1—O4ⁱⁱ	75.98 (6)	Ce1—O3—Ce1ⁱⁱ	117.57 (6)
O3—Ce1—O4ⁱⁱ	110.26 (5)	C3—O4—Ce1ⁱⁱ	94.24 (14)
O3W—Ce1—O4ⁱⁱ	73.16 (6)	O2—C1—O1	120.1 (2)
O1—Ce1—O4ⁱⁱ	143.27 (6)	O2—C1—C2	117.4 (2)
O2W—Ce1—O4ⁱⁱ	76.65 (6)	O1—C1—C2	122.5 (2)
O2ⁱ—Ce1—O4ⁱⁱ	68.32 (5)	O2—C1—Ce1ⁱ	58.39 (12)
O3ⁱⁱ—Ce1—O4ⁱⁱ	48.92 (5)	O1—C1—Ce1ⁱ	61.67 (12)
O1W—Ce1—O1ⁱ	80.87 (6)	C2—C1—Ce1ⁱ	175.81 (16)
O3—Ce1—O1ⁱ	126.38 (5)	C3—C2—C1	117.41 (19)
O3W—Ce1—O1ⁱ	145.13 (6)	C3—C2—H2A	107.9
O1—Ce1—O1ⁱ	61.54 (6)	C1—C2—H2A	107.9
O2W—Ce1—O1ⁱ	81.26 (6)	C3—C2—H2B	107.9
O2ⁱ—Ce1—O1ⁱ	48.93 (5)	C1—C2—H2B	107.9
O3ⁱⁱ—Ce1—O1ⁱ	145.80 (5)	H2A—C2—H2B	107.2
O4ⁱⁱ—Ce1—O1ⁱ	117.21 (5)	O4—C3—O3	119.7 (2)
O1W—Ce1—Cl1	74.57 (5)	O4—C3—C2	120.1 (2)
O3—Ce1—Cl1	77.74 (4)	O3—C3—C2	120.2 (2)
O3W—Ce1—Cl1	76.42 (5)	O4—C3—Ce1ⁱⁱ	61.20 (12)
O1—Ce1—Cl1	73.15 (4)	O3—C3—Ce1ⁱⁱ	60.43 (12)
O2W—Ce1—Cl1	139.90 (4)	C2—C3—Ce1ⁱⁱ	167.62 (17)
O2ⁱ—Ce1—Cl1	117.38 (4)	Ce1—O1W—H1X	120.7 (18)
O3ⁱⁱ—Ce1—Cl1	132.52 (4)	Ce1—O1W—H1Y	128.3 (18)
O4ⁱⁱ—Ce1—Cl1	143.42 (5)	H1X—O1W—H1Y	109.8 (14)
O1ⁱ—Ce1—Cl1	78.76 (4)	Ce1—O2W—H2X	114 (2)
O1W—Ce1—C3ⁱⁱ	94.47 (7)	Ce1—O2W—H2Y	116.0 (19)
O3—Ce1—C3ⁱⁱ	85.75 (6)	H2X—O2W—H2Y	110.2 (15)
O3W—Ce1—C3ⁱⁱ	64.67 (6)	Ce1—O3W—H3X	132.1 (19)
O1—Ce1—C3ⁱⁱ	130.83 (6)	Ce1—O3W—H3Y	116.4 (19)
O2W—Ce1—C3ⁱⁱ	72.81 (6)	H3X—O3W—H3Y	109 (3)

O2ⁱ—Ce1—C3ⁱⁱ	90.33 (6)	H4X—O4W—H4Y	110.0 (16)
O1W—Ce1—O1—C1	−84.6 (2)	C1ⁱ—Ce1—O3—C3	−23.8 (3)
O3—Ce1—O1—C1	46.42 (19)	O1W—Ce1—O3—Ce1ⁱⁱ	−101.07 (10)
O3W—Ce1—O1—C1	16.4 (2)	O3W—Ce1—O3—Ce1ⁱⁱ	−73.68 (8)
O2W—Ce1—O1—C1	143.9 (2)	O1—Ce1—O3—Ce1ⁱⁱ	129.82 (8)
O2ⁱ—Ce1—O1—C1	−152.87 (19)	O2W—Ce1—O3—Ce1ⁱⁱ	63.96 (7)
O3ⁱⁱ—Ce1—O1—C1	92.5 (2)	O2ⁱ—Ce1—O3—Ce1ⁱⁱ	71.47 (16)
O4ⁱⁱ—Ce1—O1—C1	138.16 (18)	O3ⁱⁱ—Ce1—O3—Ce1ⁱⁱ	0.0
O1ⁱ—Ce1—O1—C1	−123.6 (2)	O4ⁱⁱ—Ce1—O3—Ce1ⁱⁱ	−10.60 (9)
Cl1—Ce1—O1—C1	−37.46 (19)	O1ⁱ—Ce1—O3—Ce1ⁱⁱ	140.74 (6)
C3ⁱⁱ—Ce1—O1—C1	106.6 (2)	Cl1—Ce1—O3—Ce1ⁱⁱ	−153.33 (7)
C1ⁱ—Ce1—O1—C1	−139.21 (18)	C3ⁱⁱ—Ce1—O3—Ce1ⁱⁱ	−9.01 (7)
O1W—Ce1—O1—Ce1ⁱ	39.03 (11)	C1ⁱ—Ce1—O3—Ce1ⁱⁱ	119.68 (10)
O3—Ce1—O1—Ce1ⁱ	170.01 (9)	Ce1ⁱ—O2—C1—O1	−0.2 (2)
O3W—Ce1—O1—Ce1ⁱ	139.96 (7)	Ce1ⁱ—O2—C1—C2	179.99 (18)
O2W—Ce1—O1—Ce1ⁱ	−92.54 (8)	Ce1—O1—C1—O2	133.00 (19)
O2ⁱ—Ce1—O1—Ce1ⁱ	−29.27 (8)	Ce1ⁱ—O1—C1—O2	0.2 (2)
O3ⁱⁱ—Ce1—O1—Ce1ⁱ	−143.90 (7)	Ce1—O1—C1—C2	−47.2 (3)
O4ⁱⁱ—Ce1—O1—Ce1ⁱ	−98.25 (10)	Ce1ⁱ—O1—C1—C2	180.0 (2)
O1ⁱ—Ce1—O1—Ce1ⁱ	0.0	Ce1—O1—C1—Ce1ⁱ	132.79 (18)
Cl1—Ce1—O1—Ce1ⁱ	86.13 (7)	O2—C1—C2—C3	176.4 (2)
C3ⁱⁱ—Ce1—O1—Ce1ⁱ	−129.82 (8)	O1—C1—C2—C3	−3.4 (4)
C1ⁱ—Ce1—O1—Ce1ⁱ	−15.61 (7)	Ce1ⁱⁱ—O4—C3—O3	−15.7 (2)
O1W—Ce1—O3—C3	115.4 (2)	Ce1ⁱⁱ—O4—C3—C2	165.9 (2)
O3W—Ce1—O3—C3	142.8 (3)	Ce1—O3—C3—O4	163.95 (17)
O1—Ce1—O3—C3	−13.7 (2)	Ce1ⁱⁱ—O3—C3—O4	15.9 (2)
O2W—Ce1—O3—C3	−79.6 (2)	Ce1—O3—C3—C2	−17.7 (4)
O2ⁱ—Ce1—O3—C3	−72.1 (3)	Ce1ⁱⁱ—O3—C3—C2	−165.7 (2)
O3ⁱⁱ—Ce1—O3—C3	−143.5 (3)	Ce1—O3—C3—Ce1ⁱⁱ	148.1 (2)
O4ⁱⁱ—Ce1—O3—C3	−154.1 (2)	C1—C2—C3—O4	−146.9 (2)
O1ⁱ—Ce1—O3—C3	−2.8 (3)	C1—C2—C3—O3	34.7 (3)
Cl1—Ce1—O3—C3	63.1 (2)	C1—C2—C3—Ce1ⁱⁱ	−54.5 (8)
C3ⁱⁱ—Ce1—O3—C3	−152.5 (2)		

Symmetry codes: (i) −x+2, −y, −z+2; (ii) −x+1, −y, −z+2.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1X···Cl1ⁱⁱⁱ	0.94 (1)	2.20 (2)	3.0967 (18)	159 (2)
O1W—H1Y···O2ⁱᵛ	0.94 (1)	1.71 (1)	2.652 (2)	174 (3)
O2W—H2X···Cl1ⁱ	0.94 (1)	2.11 (1)	3.0416 (19)	171 (3)
O2W—H2Y···O4Wᵛ	0.94 (1)	1.94 (2)	2.816 (4)	153 (3)
O2W—H2Y···O4W	0.94 (1)	2.00 (2)	2.793 (4)	141 (3)
O3W—H3X···O4Wᵛⁱ	0.95 (1)	1.86 (1)	2.798 (2)	173 (3)
O3W—H3Y···O2Wᵛⁱⁱ	0.95 (3)	1.85 (3)	2.794 (3)	173 (3)

O4*W*—H4*X*···Cl1[ii]	0.95 (1)	2.38 (1)	3.326 (4)	176 (6)
O4*W*—H4*Y*···O4[vii]	0.95 (1)	2.26 (4)	3.083 (4)	144 (5)

Symmetry codes: (i) −*x*+2, −*y*, −*z*+2; (ii) −*x*+1, −*y*, −*z*+2; (iii) *x*, −*y*−1/2, *z*−1/2; (iv) −*x*+2, *y*−1/2, −*z*+5/2; (v) −*x*+1, −*y*, −*z*+1; (vi) −*x*+1, *y*−1/2, −*z*+5/2; (vii) *x*, *y*, *z*−1.